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Research Article

Effect of Substrate Sodium Content on Crystallization and Photocatalytic Activity of TiO₂ Films Prepared by DC Magnetron Sputtering

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The effect of sodium content of the glass support on the crystallinity of sputtered TiO₂ films and photocatalytic breakdown of ethanol has been studied. It was found that the activity of the as-deposited (amorphous) films does not depend on the type of support used. The chemical composition of the glass support does influence the activity of annealed films. When using soda-lime glass support sodium diffuses into the film upon annealing, suppressing anatase crystallization and decreasing its photocatalytic activity. To decrease the influence of sodium, soda-lime glass coated with an e-beam evaporated SiO₂ barrier layer was used with good result. A reduced sodium concentration in the film leads to well crystallized anatase after annealing. An increased photocatalytic activity was observed for these films.

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1. INTRODUCTION

In recent years, many studies have focused on titanium dioxide (TiO₂) which can be used as gas sensor [1], waveguide [2], solar energy cell [3], and photocatalyst [4]. Among the various applications of TiO₂, its photocatalytic effect has received much attention in the fields of purification and treatment of polluted water and air [5, 6]. Various air borne volatile organic compounds (VOCs) have been investigated related to industrial, traffic, and indoor pollutants. They are part of solvents which are present in indoor air in the form of paint, binders, or glues. Their slow release in small concentrations from walls, furniture, and so forth can pollute the indoor air over years. Photocatalysis with anatase TiO₂ has proven to be a very effective means of removing small concentrations of VOCs from air.

Photodegradation of organic compounds occurs when TiO₂ is illuminated by UV light ($\lambda < 387.5$ nm) in the presence of oxygen. If the correct conditions are chosen, most organic compounds should be completely degradable to water, CO₂, and mineral acids. The first step in photodegradation

is the generation of electrons and holes within the TiO₂ particles. On the TiO₂ surface •OH radicals are formed by the reaction between the valence band holes (h^+) and OH[−] groups on the hydrated catalyst surface. These hydroxyl radicals then oxidise adsorbed VOC molecules. The photogenerated conduction band electrons (e^-) are trapped by the ambient oxygen to form superoxide ions O₂[−]. The lifetimes of the electron and the hole have an influence on how efficiently they can be utilised for the above-described redox-reaction. Structural imperfections in the TiO₂ lattice generate trap sites and recombination centres, leading to a decrease of the electron and hole concentration [7, 8]. Therefore, well crystallized TiO₂ is expected to show the highest photocatalytic activity [9, 10]. Another important factor for the chemical activity of a catalyst is the number of active sites, which is expected to increase with the total available surface area and crystallinity of the photocatalyst [11]. Increasing the surface area by decreasing the particle size does not necessarily lead to a higher photocatalytic activity due to the parallel increase in defects. The density of surface hydroxyl groups, film thickness, and UV light intensity [12] are mentioned as additional

parameters influencing the photocatalytic activity of anatase TiO_2 .

Additives or impurities can also affect the crystallization and defect structure of TiO_2 , influencing its photocatalytic behaviour. In particular, sodium uptake has been found to be detrimental [13, 14], but its influence is not fully understood yet. Tada and Tanaka [15] reported that the photocatalytic activity of sol-gel TiO_2 film coated on a soda-lime glass substrate was lower than that coated on quartz plate and it was due to Na^+ ions acting as the recombination centre or disordering the crystallinity of TiO_2 . On the other hand, Nam et al. [16] claimed that the recombination centre hypothesis for Na^+ ions thermally diffused from the substrates containing Na^+ does not hold for the sol-gel TiO_2 films. Instead, Na^+ in the film affects the photocatalytic activity of the TiO_2 films through changing the particle size of anatase. To prevent the negative effect of sodium ions on the photocatalytic activity many methods such as precoating soda-lime glass with a SiO_2 barrier layer [17] or dipping the TiO_2 film in a HCl solution [18] have been reported. Recently, it has been shown that H_2SO_4 solution treatment [19] also reduces the concentration of sodium and other impurities on the surface of TiO_2 thin films and, as a result, enhances the photocatalytic activity of the film.

To apply TiO_2 as a photocatalyst for air purification it needs to be immobilised onto a carrier. Many studies have focused on TiO_2 thin films deposited by sol-gel or dip-coating methods [20]. However, these films have a rather low mechanical stability. Hard coatings can be achieved by physical or chemical vapour deposition techniques. In our case, dc magnetron sputtering from ceramic targets was used to prepare transparent nanostructured TiO_2 thin films [21–23]. This method offers many ways to improve the photocatalytic activity of TiO_2 such as controlling film microstructure or preparing composite thin films [23].

The aim of the present study is to explain the influence of sodium in the glass support on the layer crystallization and photocatalytic activity of TiO_2 thin films deposited by dc magnetron sputtering. For this purpose the thin films were deposited onto bare soda-lime glass substrate having high sodium content and onto the same substrate covered by a SiO_2 barrier layer which acts as a diffusion barrier for Na^+ ions.

2. EXPERIMENTAL

TiO_2 films were deposited by dc magnetron sputtering in a custom made vacuum chamber using a cylindrical magnetron (von Ardenne PPS50) [23, 24]. A conductive substoichiometric TiO_{2-x} ceramic target of 50 mm diameter and 3 mm thickness was used (ITME, Warsaw, Poland) [24]. Before deposition the chamber was pumped to a base pressure below 10^{-3} Pa. Sputtering was performed in pure argon at a constant power of 50 W (Huttinger PFG1500). The target-to-substrate distance was 10 cm; the deposition temperature did not exceed 325 K (self heating due to deposition). The first type of substrate was soda-lime microscope slide glass (Fiers-Roth, Belgium) containing 14.3 wt% of Na_2O . The second

support was the same microscope slide glass coated with a 40 nm SiO_2 layer using reactive electron beam evaporation. The deposition was performed in a Univex 450 vacuum chamber (Leybold) with a base pressure of 2×10^{-4} Pa. Films were deposited on unheated substrates from SiO_2 tablets (Balzers, 99, 98%) at a rate of 1.5 nm/s in 2×10^{-2} Pa of oxygen.

Previous results showed that the photocatalytic activity of TiO_2 thin films sputtered at 180 W improved with deposition pressure [23]. This pressure dependence was verified at lower deposition powers. Therefore, a rather high deposition pressure of 1.4 Pa was chosen. Increasing the deposition pressure further did not lead to an improvement of the photocatalytic activity.

A deposition time of 120 min was chosen to achieve a film thickness close to 400 nm, which was verified using a profilometer (Taylor-Hobson Talystep). After deposition samples were heat-treated in ambient air at temperatures between 533–873 K to investigate layer crystallization. This was checked by means of XRD analysis, using a diffractometer (Siemens Kristalloflex D5000) with $\text{CuK}\alpha$ radiation at 40 kV and 40 mA working in the θ - 2θ mode. XPS (Perkin Elmer PHI ESCA 5500) was used to determine the stoichiometry of the as-deposited films and the concentration of Na^+ in the annealed layers.

Measurement of the photocatalytic activity was performed in a custom-made stainless steel batch reactor with a volume of 8.75 dm³ [23]. The reaction chamber was first evacuated and then backfilled with an inert Ar/O_2 atmosphere (ratio 80 : 20 to simulate air) at 1.05×10^5 Pa. Subsequently 273 ppm ethanol (absolute PA, Panreac, Spain) were injected into the chamber and the atmosphere was stirred with a fan. The ethanol concentration was monitored with an atmospheric gas analyser containing a mass spectrometer (Pfeiffer Vacuum Omnistar). The thin films were illuminated at a distance of 15 cm with light from a mercury high-pressure short arc bulb (Osram HBO 200 W/2) set to 100 W, which passed first through an IR filter (60 mm water column). Therefore, the active peak wavelength of the UV lamp was 365 nm. The temperature during the reaction process was maintained constant at 313 K. The illuminated thin film area was 31 mm by 25 mm.

3. RESULTS AND DISCUSSION

All as-deposited TiO_2 thin films were found to be XRD amorphous and stoichiometric independent of the type of glass support used. For annealed films, on the other hand, the chemical composition of the glass support strongly influenced the crystallinity and photocatalytic activity. For films deposited on soda-lime glass the lowest crystallization temperature was 773 K, and the reflections observed in the XRD spectrum were very weak (Figure 1), indicating poor film crystallinity. At 773 K only reflections from anatase could be seen, with the (101) reflection being stronger than expected from the powder spectrum. At 823 K very weak (100) reflection from rutile appeared, which became stronger with increasing annealing temperature.

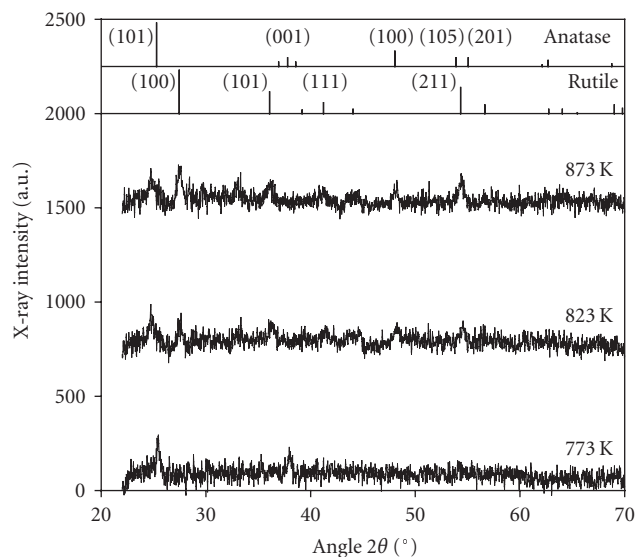


FIGURE 1: X-ray diffraction spectra of TiO_2 thin films deposited on bare soda-lime glass. The films were sputter deposited at 50 W, 1.4 Pa and annealed for 1 h. Included are the powder spectra of anatase (ASTM 21-1272) and rutile (21-1276).

For soda-lime glass coated with a 40 nm SiO_2 barrier layer anatase crystallization occurred upon annealing at 573 K (Figure 2). The observed reflections were much stronger and there was a strong (001) preferential orientation. The maximum peak intensity was almost reached at 623 K; there was only a small increase in peak intensity for the film annealed at 873 K. For the films deposited onto a SiO_2 barrier layer no rutile crystallization was observed at a temperature of 873 K as compared to the films deposited on pure soda-lime glass, where rutile crystallization was observed at temperatures above 823 K. This shows that it is the uptake of sodium into the thin films that resulted in the low crystallization temperature of rutile.

XPS was performed on the surface of thin films deposited onto both substrates and annealed at temperatures of 623 K and 873 K. In Table 1 the atomic concentration of Na and Si are shown (balanced to 100% with O and Ti). The results reveal that there is a strong uptake of sodium (> 12 at%) in the film deposited onto soda-lime glass and annealed at a temperature of 623 K. The sodium uptake of the films deposited onto SiO_2 barrier layer and annealed at the same temperature was four times lower. One can see that the 40 nm SiO_2 layer loses its effectiveness as barrier at very high annealing temperatures (873 K). However, the sodium uptake through the barrier layer was only about half of the value observed for the soda-lime substrate at lower annealing temperature.

There are different views reported on the crystallization of TiO_2 in the presence of sodium ions. Schroeder [25] thought that annealing TiO_2 films on soda-lime glass resulted in the formation of brookite or sodium titanate ($\text{Na}_2\text{O} \times \text{TiO}_2$). Takahashi et al. [26] found that anatase was formed at a thickness of more than 50 nm, whereas amorphous TiO_2 was formed at thickness of less than 50 nm when

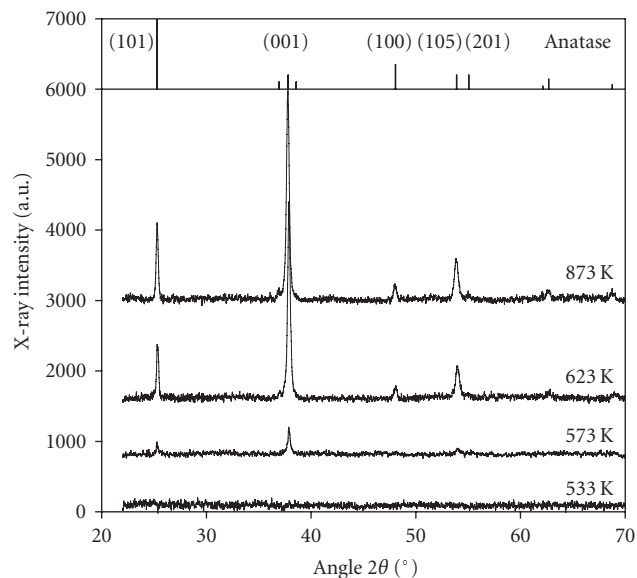


FIGURE 2: X-ray diffraction spectra of TiO_2 thin films deposited on soda-lime glass with a SiO_2 barrier layer. The films were sputter deposited at 50 W, 1.4 Pa and annealed for 1 h.

TABLE 1: Na and Si concentrations on the surface of annealed TiO_2 thin films, as observed with XPS.

Substrate	Na1s (at%)	Si2p (at%)
Soda-lime glass (623 K)	12.22	0.31
Soda-lime glass with SiO_2 barrier (623 K)	3.17	0.91
Soda-lime glass with SiO_2 barrier (873 K)	7.74	2.04

annealing thin films on sodium containing glass. Paz and Heller [27] stated that sodium could diffuse into the nascent TiO_2 film and prevent formation of photoactive anatase. Yu and Zhao [17] found that a SiO_2 layer introduced at the interface between soda-lime glass and the nascent TiO_2 film retarded diffusion of sodium ions from soda-lime glass into the thin film. When the SiO_2 layer was thicker than 300 nm, diffusion of sodium was prevented and anatase crystallization was observed. Our XPS and XRD results showed that the crystallization of anatase was dependent on the sodium concentration in the TiO_2 films. In the case of soda-lime glass, rutile appeared at 823 K, while for pure TiO_2 samples anatase begins to transform to rutile at 973 K [28]. This means that a high concentration of sodium favours the decrease of the rutile crystallization temperature.

Reaction rates for the photocatalytic breakdown of ethanol were calculated from the initial slope of the curves of the ethanol concentration versus time. Their dependence on annealing temperature and substrate type is shown in Figure 3. For the soda-lime glass substrate the as-deposited film (XRD amorphous) shows the highest activity. There is a strong

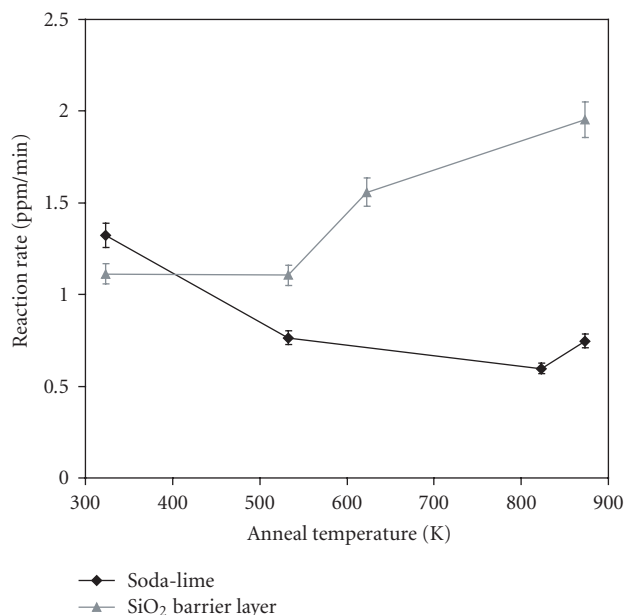


FIGURE 3: Dependence of the photocatalytic breakdown reaction rate of TiO_2 thin films on the anneal temperature for the two different substrate types. The reaction rate of the photocatalytic breakdown of 273 ppm ethanol was determined from the slope of the concentration versus time measurement.

decrease in reaction rate, an effect which increases with annealing temperature.

This finding suggests that Na^+ ions act as the recombination centre of the h^+e^- pairs, an effect which increases with higher Na^+ diffusion at higher annealing temperatures, leading to the significant reduction of the photocatalytic activity. Disordering the crystallinity of TiO_2 is a parallel effect of Na^+ ion presence. This is in accordance with previous results for films sputtered at 180 W using the same experimental setting [23]. No such decrease in reaction rate is observed for films deposited onto SiO_2 barrier layer coated soda-lime glass. Here the reaction rate remains constant until film crystallization begins at temperatures above 573 K. One can see that the photocatalytic activity increases with increasing crystallinity. The photocatalytic activity of films deposited onto a SiO_2 barrier layer on soda-lime glass at 623 K shows a strong increase; annealing the films at a temperature of 873 K results in an even higher photocatalytic activity. Interestingly, the sodium uptake at this temperature is higher than at 623 K but still almost twice lower than for the film deposited directly on soda-lime glass and annealed at 623 K. It was already proposed in a previous publication [23] that there are two competing factors influencing the photocatalytic efficiency of annealed TiO_2 thin films deposited onto sodium containing glass. The first factor was sodium diffusion, leading to an increased sodium uptake with increasing annealing temperature. The second factor was the degree of crystallization which was expected to improve with annealing temperature. The results in this paper show that sodium uptake does have a detrimental effect on the photocatalytic efficiency of ethanol breakdown when comparing films annealed at low

temperatures (533 K) where no crystallization has yet occurred (Figure 3), confirming the first part of the hypothesis. With the films deposited onto soda-lime glass coated with a SiO_2 barrier layer, the sodium diffusion is suppressed and the crystallization of anatase is seen to improve substantially with anneal temperatures above 623 K (Figure 2) increasing the photocatalytic activity strongly (Figure 3). It is noteworthy that Si was observed in TiO_2 films for both substrates examined here (Table 1). Although the amount was smaller than that of Na, its content increased as the annealing temperature increased. It has been reported that the presence of SiO_2 in TiO_2 prevents the transformation of anatase to rutile [29] by suppressing the crystal growth; this effect, and the influence of Si on the photocatalytic activity, is subject of further investigations.

4. SUMMARY

The effect of the sodium content of the glass support on the crystallinity and photocatalytic activity of TiO_2 thin films deposited by dc magnetron sputtering was investigated. All as-deposited films were found to be XRD amorphous and it was found that the reaction rate of the photocatalytic breakdown of ethanol in simulated air was similar for all types of substrate, being between 1.1 and 1.45 ppm/min.

For annealed films it was found by XPS analysis that the sodium uptake is much higher for films deposited onto soda-lime glass (> 12 at%) than for films deposited onto e-beam evaporated 40 nm thick SiO_2 barrier layer on soda-lime glass. This resulted in a difference in crystallization behaviour upon annealing. Films deposited onto soda-lime glass needed high crystallization temperatures of 773 K, crystallization was poor and at higher temperatures no improvement but formation of the rutile phase was observed. The annealed films showed a reduced photocatalytic activity compared to the as-deposited one. Films deposited on the SiO_2 barrier layer showed good crystallization at temperatures above 573 K, having a preferred (001) orientation. No sign of rutile formation up to temperatures of 873 K was observed. Annealing of these films did not lead to deterioration of the photocatalytic activity, but improved it strongly, yielding a value of 1.95 ppm/min at anneal temperature of 873 K for a TiO_2 film deposited onto a SiO_2 barrier layer.

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